KINETICS OF BITUMINOUS COAL CHAR GASIFICATION WITH GASES CONTAINING STEAM AND HYDROGEN

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INTRODUCTION

Correlations to quantitatively define the effects of pertinent intensive variables on the kinetics of coal or coal char gasification reactions are necessary for the rational design of commercial systems to convert coal to pipeline gas. The available information, which can be applied to the development of such correlations is relatively limited, particularly because the data reported from many studies conducted with integral contacting systems reflect, in part, undefined physical and chemical behavior peculiar to the specific experimental systems used. Although some differential rate data have been obtained with various carbonaceous materials, they cover only narrow ranges of the conditions potentially applicable to commercial gasification systems.

During the last several years, the Institute of Gas Technology (IGT) has been conducting a continuing study to obtain fundamental information on the gasification of coals and coal chars, which could be used, along with selected information in the literature, to develop engineering correlations which quantitatively define the effects of intensive variables on gasification rates over a wide range of conditions applicable to a variety of conceivable gasification processes. The models and correlations developed at the present time are primarily applicable to bituminous coal chars prepared at mild or severe conditions in either inert or oxidizing atmospheres. Although we have achieved some success in applying these correlations to the gasification of subbituminous and lignite coals for limited ranges of conditions, the gasification kinetics of such materials have shown wide deviations from predictions of the correlations at lower temperatures and during initial stages of gasification.

The objective of this paper is a) to discuss the models which have been developed; b) to present the correlations derived from these models; and c) to demonstrate the consistencies between predictions of these correlations and various experimental gasification data obtained primarily with bituminous coal chars. We obtained the experimental information used in developing the models from two main sources. Initial development of the model for application to the gasification of devolatilized coal char in hydrogen and steam-hydrogen mixtures was based both on data obtained in an extensive study conducted at IGT with a high-pressure thermobalance apparatus and on differential rate data obtained by investigators at the Consolidation Coal Company for the gasification of Disco char in a small-scale fluid bed. [9, 18, 19] Then, the model was extended to apply to the gasification of char containing volatile matter and to gasification with gases containing carbon monoxide, carbon dioxide, and methane, as well as steam and hydrogen, using data obtained primarily in the thermobalance study.

The thermobalance has been a particularly useful tool for obtaining fundamental gasification information, since with this type of apparatus, gasification rates can be measured at constant, well-defined, environmental conditions. Since a major amount of the information used in the formulation of the kinetic models developed, was based on data obtained in several hundred tests conducted with the thermobalance, a brief description of this apparatus is given below.

EXPERIMENTAL

The thermobalance is an apparatus capable of continuously weighing a coal sample which is undergoing reaction in a gaseous environment of desired composition at a constant pressure. The temperature can either be kept constant or varied. (10 °F/min is the maximum rate for the apparatus used at IGT.) The nature of gas-solid contacting with the apparatus used in this study is shown in Figure 1. The coal sample is contained in the annular space of a wire-mesh basket bounded on the inside by a hollow, stainless-steel tube and on the outside by a wire mesh screen. To facilitate mass and heat transfer between the bed and its environment, the thickness of the bed is only 2-3 particle diameters when using −20+40 USS sieve-size particles. Gas flow rates used with this system are sufficiently large relative to gasification rates, that gas conversion is limited to less than 1 % for devolatilized coal char.
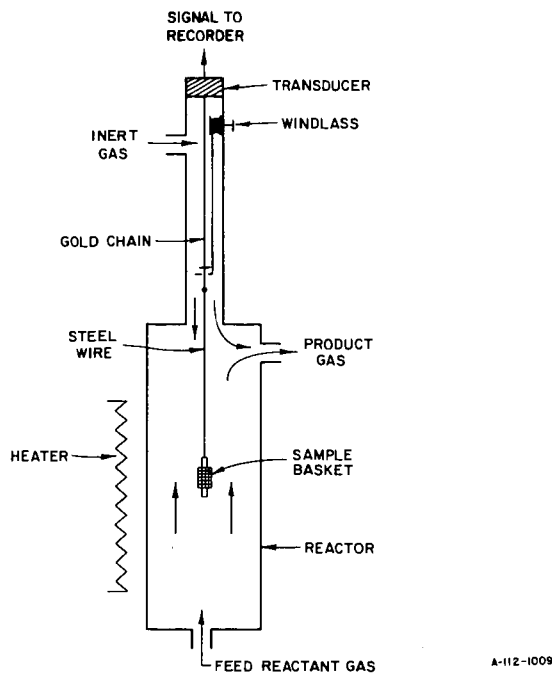
Figure 1. DIAGRAM OF THERMOBALANCE REACTOR

   The following is a typical test procedure: The wire mesh basket is
initially in an upper cooled portion of the reactor in which a downward, inert
gas flow is maintained.   During this time the desired temperature and pressure
conditions are established in a lower heated portion of the reactor in the
presence of a flowing gas.   A test is initiated by lowering the basket into
the heated reaction zone, a procedure which takes 5-6 seconds.   Theoretical
computation indicates that about 2 minutes are required for the sample to
achieve reactor temperature, as measured by several thermocouples
surrounding the basket in the reaction zone.   This computation is reasonably
corroborated by various kinetic indications and by the behavior of the thermo-
couples in reattaining their preset temperatures.   The sample is kept in the
heated portion of the reactor for the specified time while its weight is con-
tinuously recorded.   The test is terminated by raising the basket back to the
upper, cooled portion of the reactor.

230

During a test, the dry feed gas flow rates are measured by orifice meter and the dry product gas flow rates by a wet-test meter. Periodic samples of product gas are taken to determine the dry gas' composition by mass spectrograph. Feed and product steam flow rates are measured by gravimetric means, and the solids residues are analyzed for total carbon and hydrogen.

Figure 2 shows some typical, smoothed, weight loss-versus-time characteristics obtained using an air-pretreated hvAb Pittsburgh coal char from the Ireland mine. These curves are discussed in more detail in a subsequent
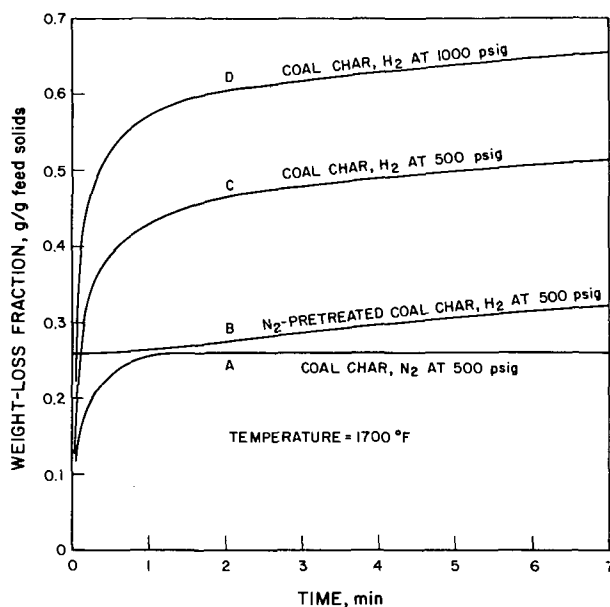
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Figure 2. TYPICAL WEIGHT-LOSS CURVES OBTAINED WITH THE
HIGH-PRESSURE THERMOBALANCE FOR GASIFICATION OF
AIR-PRETREATED IRELAND MINE COAL CHAR IN
HYDROGEN AND IN NITROGEN

section of this paper. The composition of the coal char, used extensively in the experimental study, is given in Table 1.

Table 1. COMPOSITION OF AIR-PRETREATED hvAb
PITTSBURGH NO. 8 COAL CHAR (Ireland Mine)

Ultimate Analysis, dry	wt %
Carbon	71.1
Hydrogen	4.26
Oxygen	8.85
Nitrogen	1.26
Sulfur	3.64
Ash	10.89
Total	100.00

Proximate Analysis, dry ~~as received~~

Fixed Carbon	60.7
Volatile	28.4
Ash	10.9
Total	100.0

DESCRIPTION OF KINETIC MODELS

When a coal or coal char containing volatile matter is initially subjected
to an elevated temperature, a series of complex physical and chemical changes
occur in the coal's structure accompanied by thermal pyrolysis reactions,
which result in devolatilization of certain coal components.   The distribution
of the evolved products of the reactions, which initiate at less than 700 °F and
can be considered to occur almost instantaneously at temperatures greater
than 1300 °F, is generally a function of the temperature, pressure, and gas
composition existing during devolatilization and of the subsequent thermal and
environmental history of the gaseous phase (including entrained liquids) prior
to quenching.

When devolatilization occurs in the presence of a gas containing hydrogen
at an elevated pressure, in addition to thermal pyrolysis reactions, coals or
coal chars containing volatile matter also exhibit a high, although transient,
reactivity for the formation of methane. Although some investigators have
suggested that this process occurs concurrent with thermal pyrolysis reactions,

232

results of studies made with a greater time resolution indicated that this rapid-rate methane formation occurs at a rate which is at least an order of magnitude slower than devolatilization.[7, 17] In this sense it occurs consecutively to devolatilization.

The amount of carbon gasified to methane during the transient period of high reactivity increases significantly with increases in hydrogen partial pressure.[7, 13, 17] Experimental evidence indicates that, at sufficiently high hydrogen partial pressures, virtually all of the carbon not evolved during devolatilization can be gasified to methane during a very short time period by this process.[13] This is contrary to some proposed models, which assume that only a limited amount of carbon can be gasified in this reaction stage, regardless of the hydrogen partial pressure.[3, 16]

At temperatures greater than 1700°F, the transient reactivity for rapid-rate methane formation exists for a very short period of time. For coals, or coal chars prepared in inert atmospheres, this period lasts only seconds or less.[13] IGT's studies suggest that for air-pretreated coal chars, this period is more extended, although the total amounts of carbon which can be gasified by this process at a given temperature and hydrogen partial pressure, are comparable for coals and coal chars prepared at sufficiently low temperatures either in inert gas or in air.

After the devolatilization and rapid-rate methane formation stages are completed, char gasification occurs at a relatively slow rate, and various models to describe the gasification kinetics of this material for various limited ranges of conditions have been proposed. The differential rates of reaction of devolatilized coal chars are a function of temperature, pressure, gas composition, carbon conversion, and "prior history."

General Assumptions in the Development of Models

The models developed in this study for the quantitative description of coal char gasification kinetics assume that the overall gasification process occurs in three consecutive stages: 1) devolatilization, 2) rapid-rate methane formation, and 3) low-rate gasification. The reactions in these three stages are independent. Further, a feed coal char contains two types of carbon, volatile carbon and base carbon.

233

Volatile carbon can be evolved solely by thermal pyrolysis, independent of the gaseous medium. The distribution of evolved products derived from the volatile carbon fraction is not defined in the model. In any application of the model to an integral contacting system, the devolatilization products are estimated by extrapolation or interpolation of yields obtained in pilot-scale fluid or moving-bed systems. This procedure can be applied for narrow ranges of conditions and only for very similar contacting systems.

Base carbon remains in the coal char after devolatilization is complete. This carbon can be subsequently gasified either in the rapid-rate methane formation stage or in the low-rate gasification stage.

A quantitative estimation of the initial amounts of volatile and base carbon is made from standard analyses of the feed coal char. The following definition has been made:

C_v (volatile carbon), g/g of feed coal = C_t^o (total carbon), g/g of feed coal

$$- C_b^o \text{ (base carbon), g/g of feed coal} \quad (1)$$

where C_t^o represents the total carbon in the feed coal char obtained from an ultimate analysis and C_b^o represents the carbon in the "fixed carbon" fraction of the feed coal as determined in a proximate analysis. It is emphasized that C_b^o does not equal the fixed carbon fraction, since the fixed carbon fraction includes, in addition to carbon, other organic coal components not evolved during standard devolatilization.

Experimental results from thermobalance or free-fall tests conducted at IGT indicate that the assumption of a constant volatile carbon fraction is valid for coal heat-up rates as high as 200 °F/s. However, other studies conducted with extremely rapid heat-up rates (10^4 to 10^7 °F/s) have shown that quantities of carbon evolved during thermal pyrolysis can exceed the volatile carbon fraction defined in this model.[6, 11] An allowance for the increase in evolved carbon would, therefore, have to be made in systems employing such high heating rates.

The base carbon conversion fraction, X, is defined as:

$$X = \frac{\text{base carbon gasified}}{\text{base carbon in feed coal char}} = \frac{C_b^o - C_b}{C_b^o} \quad (2)$$

where

C_b = base carbon in coal char at an intermediate level of gasification, g/g feed coal char

When making a kinetic analysis of the thermobalance data, it was necessary to relate the measured values of weight-loss fraction, $\Delta W/W_o$, to the base carbon conversion fraction, X. When devolatilization is complete, essentially all of the organic oxygen has been gasified. Thereafter, additional weight loss, which primarily results from gasification of the base carbon, is accompanied by the evolution of a constant fraction of noncarbon components in the coal such as nitrogen, hydrogen, and sulfur. Estimates of an average value of the fraction of noncarbon components gasified along with the base carbon for each type of coal char tested, have been based on analyses of char residues obtained in thermobalance and pilot-scale fluid-bed tests. With this simplifying assumption, the following relationships result:

$$C_b^o = (1 - V - A)(1 - \gamma) \tag{3}$$

and

$$C_b = C_b^o - \left[(\Delta W/W_o) - V\right](1 - \gamma) \tag{4}$$

where

V = volatile matter in feed coal char (including moisture), g/g feed coal char

A = nongasifiable matter in feed coal char (including ash and some sulfur), g/g feed coal char

γ = noncarbon matter evolved along with base carbon, g/g base carbon evolved

Thus, from Equations 2, 3, and 4 —

$$X = \frac{(\Delta W/W_o) - V}{1 - V - A} \tag{5}$$

The results shown in Figure 2 can be interpreted by the three reaction stages defined above. Curve A corresponds to a test in which air-pretreated Ireland mine coal char was exposed to a nitrogen atmosphere at a pressure of 500 psig. During the first minute when the sample is heating up in the

235

thermobalance, the weight loss corresponds to the evolution of volatile matter. After this period, no further significant weight loss occurs. The total weight loss of approximately 26 % corresponds closely to the volatile matter in the feed coal char obtained by standard proximate analysis. Within the context of the three reaction stages defined, weight loss in this test occurs entirely in the devolatilization stage, where all of the volatile carbon has been gasified; all of the base carbon remains in the devolatilized coal char. When the char resulting from this test is then exposed to hydrogen at 500 psig (curve B), the reaction of the hydrogen with base carbon to form methane results in further weight loss. This reaction, which takes place at a much lower rate than devolatilization, occurs in the low-rate gasification stage. With this particular sample, there was no reaction in the rapid-rate methane formation stage because the reactivity of the coal char in this stage was destroyed during prolonged exposure to nitrogen.

Weight loss as a result of the reaction in the rapid-rate methane formation stage is illustrated by curve C, where a sample of the original coal char was exposed only to hydrogen at 500 psig with no initial exposure to nitrogen. There is a weight loss during the first minute of this test which is considerably greater than the corresponding weight loss obtained during this period when the coal char was exposed to nitrogen (curve A). The difference in the amount of weight loss between curves C and A during the first minute, or so, is caused by gasification of base carbon in the rapid-rate methane formation stage. Weight losses of the magnitude exhibited by curve B during this initial period are negligible. This is consistent with the assumption that base carbon gasification in the rapid-rate methane formation stage and in the low-rate gasification stage occur consecutively.

Curve D is qualitatively similar to curve C, except that there is a greater weight loss from rapid-rate methane formation resulting from the higher hydrogen pressure.

236

Correlations for Rapid-Rate Methane Formation Stage

The amount of base carbon gasified during the rapid-rate methane formation stage can be estimated by the base carbon conversion level, X_R, obtained from weight loss-versus-time characteristics 2 minutes after a sample is lowered into the reactor. As indicated previously, this corresponds to the time required for coal heat-up. During this period negligible conversion occurs in the low-rate gasification stage, although devolatilization and rapid-rate methane formation reactions should be complete at temperatures above approximately 1500 °F. Values of X_R have been correlated with hydrogen partial pressure, P_{H_2}, according to the following expression for data obtained in tests conducted at a variety of conditions:

$$M(X_R) = \int_0^{X_R} \frac{\exp{(+\alpha X^2)}\,dX}{(1-X)^{2/3}} = 0.0092\, f_R\, P_{H_2} \qquad (6)$$

where

P_{H_2} = hydrogen partial pressure, atm

f_R = relative reactivity factor for rapid-rate methane formation dependent on the particular carbonaceous solid. (Defined as unity for air-pretreated Ireland mine coal char.)

α = kinetic parameter dependent on gas composition and pressure

The value of α in the above expression is approximately 0.97 for tests conducted in pure hydrogen or in hydrogen-methane mixtures, and is approximately equal to 1.7 for a wide variety of gas compositions containing steam and hydrogen. This parameter will be discussed in greater detail in a later section on the low-rate gasification stage. It is of interest here, however, that for the case where $\alpha = 0.97$, then $M(X_R) \cong -\ln(1-X_R)$.

In Figure 3, a plot of the function, $M(X_R)$, versus hydrogen partial pressure, P_{H_2}, for a number of tests conducted on the thermobalance with air-pretreated Ireland mine coal char, shows the good agreement between these data and the correlation form given in Equation 6. Equation 6 also appears to be reasonably applicable to the gasification of some coals, as well as to coal chars.

237
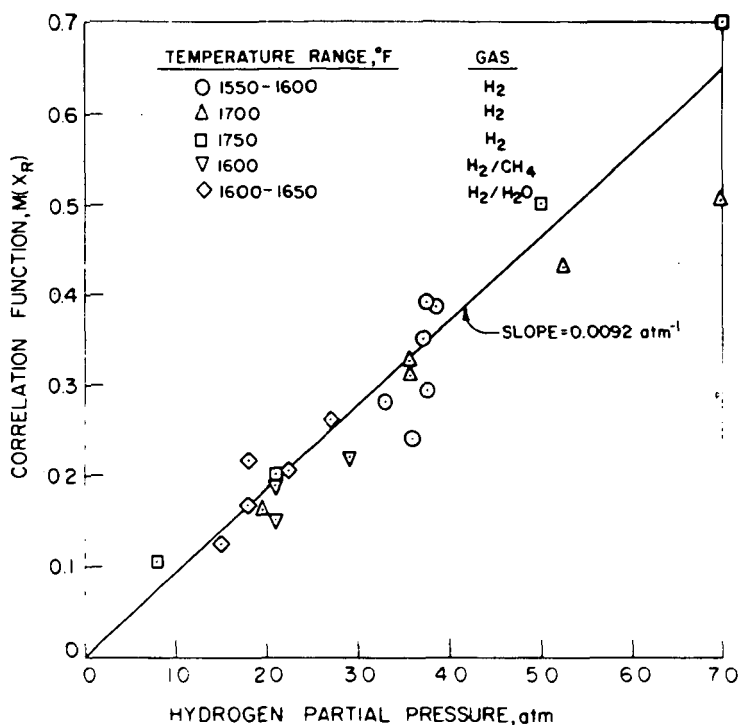
Figure 3. CORRELATION OF BASE CARBON CONVERSION FOR
GASIFICATION OF AIR-PRETREATED IRELAND MINE
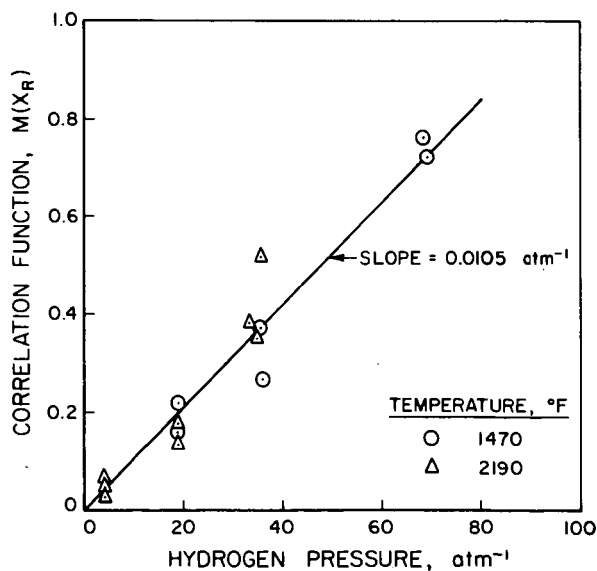COAL CHAR IN THE RAPID-RATE METHANE FORMATION STAGE

Data obtained by Birch, et al., [1] for the hydrogenation of Brown coal in a
fluid bed and by Hiteshue, et al., [10] for the hydrogenation of a hvAb Pittsburgh
coal in a fixed bed are given in Figures 4 and 5. Details of the procedures
used in treating the data from these two investigations have been previously
described.[14] It is of practical interest that relatively small variations in
values of f_R are exhibited by the different materials considered. Similar
small degrees of variation have also been noted for several other bituminous
coal chars tested at IGT using the thermobalance.

The gasification of base carbon in the rapid-rate methane formation stage
is apparently only dependent on hydrogen partial pressure   and is not de-
pendent on the partial pressures of other gaseous species normally present
in gasifying atmospheres. This is partly indicated in Figure 3 for tests

238
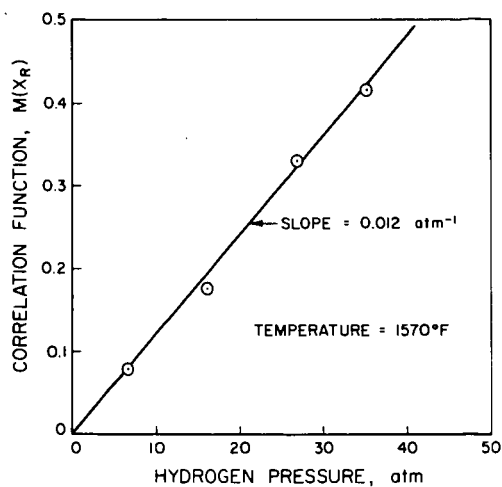
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Figure 4. CORRELATION OF BASE CARBON CONVERSION FOR
GASIFICATION OF BROWN COAL IN A FLUID BED IN THE
RAPID-RATE METHANE FORMATION STAGE[1]

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Figure 5. CORRELATION OF BASE CARBON CONVERSION FOR
GASIFICATION OF hvAb PITTSBURGH COAL IN A FIXED BED
IN THE RAPID-RATE METHANE FORMATION STAGE[10]

239

conducted with hydrogen-methane and hydrogen-steam mixtures, and has also been observed with synthesis-gas mixtures. In a system containing no hydrogen, no evolution of base carbon occurs except through gasification in the low-rate gasification stage. In Figure 6, this effect is illustrated for tests conducted with pure steam. After the first few minutes, there is no difference in the weight-loss traces for a sample of air-pretreated coal char initially lowered into a steam atmosphere, and one which was devolatilized in nitrogen prior to being exposed to the steam atmosphere. This behavior can be compared to results shown in Figure 2 for similar tests conducted in hydrogen.

COAL CHAR, H_2O AT 500 psig

NITROGEN-PRE-TREATED COAL CHAR, H_2O AT 500 psig

COAL CHAR, N_2 AT 500 psig
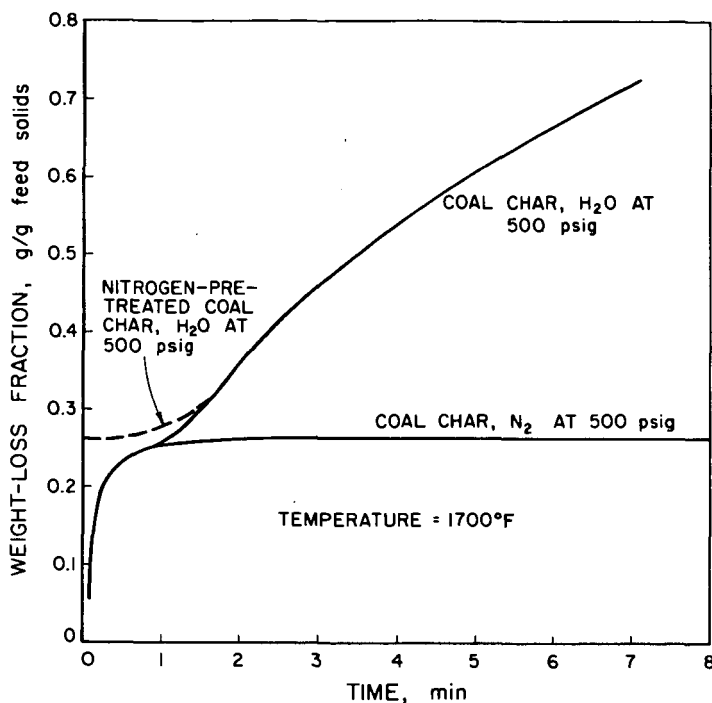
TEMPERATURE = 1700°F

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Figure 6. WEIGHT-LOSS CURVES OBTAINED IN HIGH-PRESSURE THERMOBALANCE FOR GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN STEAM AND IN NITROGEN

Although the effects of pretreatment temperature on reactivity in the rapid-rate methane formation stage have not been systematically studied in this investigation, some indication is apparent from the results given in Figure 7. It shows total weight losses for materials subjected to different pretreatments in nitrogen obtained after gasification of air-pretreated coal char in hydrogen for 1 hour. Below 1000 °F, no effect of the nitrogen pretreatment is apparent on subsequent weight loss in hydrogen. Above this temperature, however, the total weight loss for materials initially exposed to nitrogen tends to decrease with increasing temperature, and above approximately 1500 °F, no rapid-rate methane formation occurs with these materials.

The correlation described by Equation 6 was developed based on data obtained from thermobalance tests conducted above 1500 °F, where coal char samples were submitted to rather specific heat-up rates characteristic of the experimental apparatus (approximately 30 °F/s). The fact that this correlation appears to apply for data obtained in other experimental systems where heat-up rates as high as 200 °F/s were employed, suggests that, within a limited range of heat-up rates, base carbon conversion in the rapid-rate methane formation stage is independent of heat-up rate for final temperatures greater than 1500 °F. This conclusion only applies for the case where reaction in the rapid-rate methane formation stage goes to completion. At sufficiently low temperatures, the amount of base carbon conversion which can be attributed to rapid-rate methane formation, is less than that which would be predicted by Equation 6, even for exposure to hydrogen for periods as long as 1 hour. This is apparent from the results shown for curve A in Figure 7.

Data obtained in a series of experiments conducted at lower temperatures, such as those illustrated in Figure 7, have been correlated using a more detailed model to describe the rapid-rate methane formation process prior to the completion of this reaction. This model is described in a previous publication.[14] It is of interest here, however, to point out certain characteristics of this model which rationalize the independence of total base
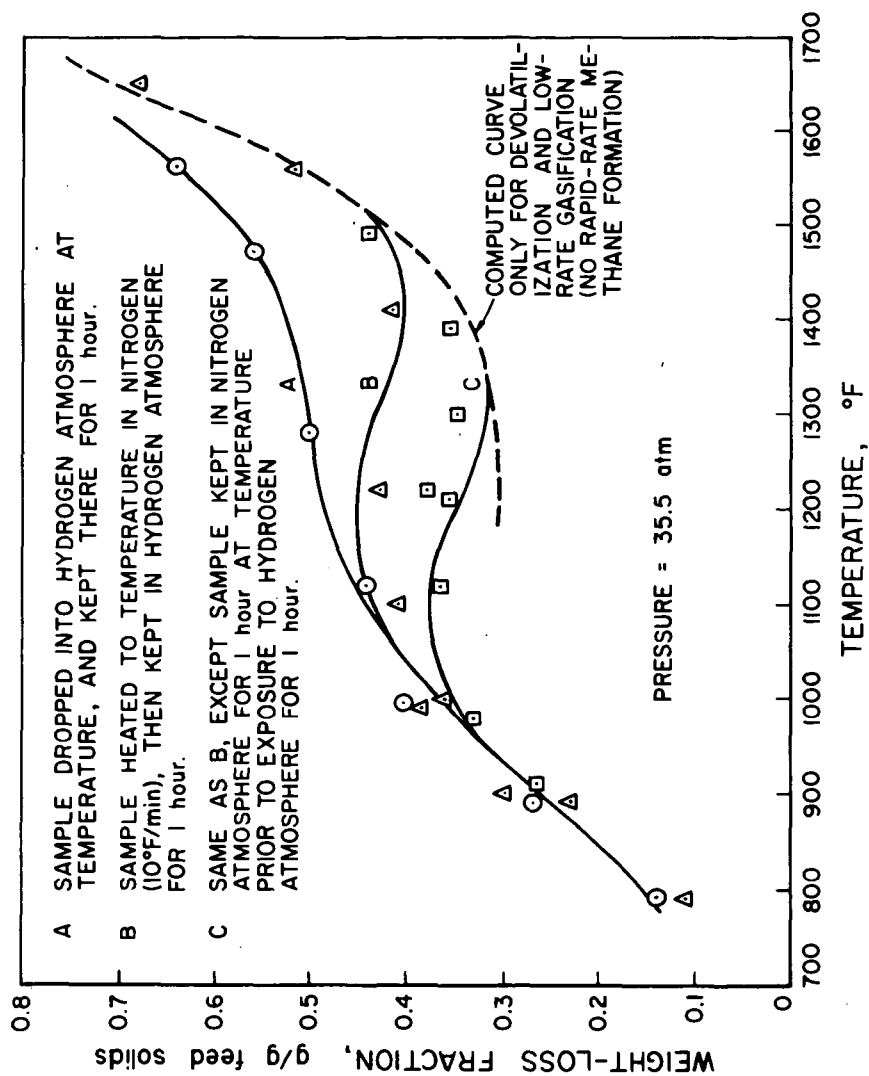
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Figure 7. EFFECT OF PRIOR EXPOSURE TO NITROGEN ON GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN THE RAPID-RATE METHANE FORMATION STAGE

carbon conversion in the rapid-rate methane formation stage from heating rate and final temperature for tests conducted above 1500 °F. The following critical steps assumed in the model relate to this range of conditions:

$$A_o \rightarrow A_* \tag{7}$$

$$A_* \rightarrow B \tag{8}$$

$$\text{base carbon + hydrogen} \xrightarrow{A_*} \text{methane} \tag{9}$$
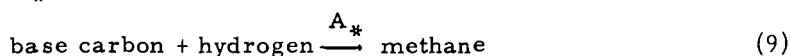
This model, which is qualitatively similar to one proposed by Mosely and Patterson,[13] assumes that the coal char initially forms an active intermediate, A_*, (Equation 7) which catalyzes the reaction between base carbon and gaseous hydrogen to form methane (Equation 9). This reaction, however, competes with a reaction in which A_* deactivates to form the inactive species, B (Equation 8).

The following expression is assumed to describe the rate of reaction in Equation 9:

$$dX/dt = f_R k_3(T) P_{H_2} (1 - X)^{2/3} \exp(-\alpha X^2) N_{A_*} \tag{10}$$

where

$k_3(T)$ = rate constant dependent on temperature, T

N_{A_*} = concentration of species, A, mol /mol of base carbon

t = time

The rates of reactions in Equations 7 and 8 are assumed to be first order, leading to the expression —

$$d(N_{A_*} + N_{A_o})/dt = - k_2(T) \cdot N_{A_*} \tag{11}$$

where,

$k_2(T)$ = rate constant, dependent on temperature

N_{A_o} = concentration of species, A_o, mol /mol base carbon

243

Combining Equations 10 and 11 leads to the expression —

$$\frac{dX}{d\left(N_{A_*} + N_{A_o}\right)} = -f_R \frac{k_3(T)}{k_2(T)} P_{H_2}(1 - X)^{2/3} \exp(-\alpha X^2) \qquad (12)$$

If, then, it is assumed that the ratio $k_3(T)/k_2(T)$ is independent of temperature and is equal to β, then Equation 12 can be integrated to yield the following expression for the condition at which all of the species A_o has been converted to B.

$$M(X_R) = \int_0^{X_R} \frac{\exp(\alpha X^2)\, dX}{(1 - X)^{2/3}} = f_R \beta \cdot N_{A_o}^o P_{H_2} \qquad (13)$$

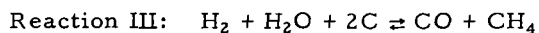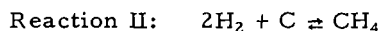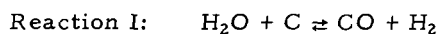Comparing this expression with Equation 6 indicates that $\beta N_{A_o}^o = 0.0092$ atm^{-1}. Since no definition of the temperature history was required in the development of Equation 13, the suggested model indicates that the amount of base carbon conversion to methane during the rapid-rate methane formation step is independent of heat-up rate or temperature level when the intermediate, A, has been completely deactivated.

Correlations for Low-Rate Gasification Stage

For practical purposes, coal chars undergo low-rate gasification only after the devolatilization and rapid-rate methane formation reactions are completed. Results obtained with the thermobalance indicate that, at temperatures greater than 1500°F, char reactivity over a major range of carbon conversion in the low-rate stage is substantially the same whether devolatilization occurs in nitrogen, or in a gasifying atmosphere at the same conditions. Therefore, this study treats low-rate char gasification as a process essentially independent of devolatilization conditions, with one important exception: The temperature of devolatilization, since it has been shown in this study as well as by Blackwood[2] that the reactivity of a char at a given temperature, T, decreases with increasing pretreatment temperature, T_o, when $T_o > T$. This effect is quantitatively represented in the correlations presented below. However, the model adopted does not account for pretreatment effects on gasification during initial stages of char gasification, which

occur particularly at gasification temperatures less than 1600 °F. At these lower temperatures, specific pretreatment conditions such as gas atmosphere and time of pretreatment produce somewhat complex effects during subsequent gasification for base carbon conversions of less than 10 %. [8] These limitations have no practical significance in using the simplified model developed to describe coal char gasification kinetics at higher temperatures, or for base carbon conversion levels sufficiently greater than 10 %.

The gasification data of Zielke and Gorin[18, 19] and Goring, et al., [9] obtained for fluid-bed gasification of Disco char, as well as the bulk of data obtained in IGT's studies with the high-pressure thermobalance and pilot-scale fluid beds, were used to evaluate parameters in a quantitative model developed to describe coal char gasification kinetics over a wide range of conditions in the low-rate gasification stage. Three basic reactions were assumed to occur in gases containing steam and hydrogen:

Reaction I: $H_2O + C \rightleftarrows CO + H_2$

Reaction II: $2H_2 + C \rightleftarrows CH_4$

Reaction III: $H_2 + H_2O + 2C \rightleftarrows CO + CH_4$

Reaction I is the conventional steam-carbon reaction, which is the only one that occurs in pure steam at elevated pressures[*] or with gases containing steam at low pressure. Although, at elevated temperatures this reaction is affected by thermodynamic reversibility only for relatively high steam conversions, the reaction is severely inhibited by the poisoning effects of hydrogen and carbon monoxide at steam conversions far removed from equilibrium for this reaction. Some investigators have also noted inhibition by methane.

Reaction II, the only reaction that could occur in pure hydrogen or in hydrogen-methane mixtures, greatly depends on the hydrogen partial pressure. Many investigators have found that, at elevated pressures, the rate of this reaction is directly proportional to the hydrogen partial pressure.

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[*] Although some methane has been detected in gaseous reaction products when gasification is conducted with pure steam, it is uncertain whether this methane results from the direct reaction of steam with carbon or from the secondary reaction of hydrogen, produced from the steam-carbon reaction, with the carbon in the char.

The stoichiometry of Reaction III limits its occurrence to systems in which both steam and hydrogen are present. Although this reaction is the stoichiometric sum of Reactions I and II, this model considers it to be a third independent gasification reaction. This reaction, arbitrarily assumed to occur in the development of this model to facilitate correlation of experimental data, has been suggested by Blackwood and McGrory[4] as being necessary in such a system. Curran and Gorin[5] also assumed this reaction to correlate kinetic data for gasification of lignite at 1500 °F in steam-hydrogen-containing gases.

The correlations developed in this study to describe kinetics in the low-rate gasification stage are summarized as follows:

$$dX/dt = f_L \, k_T \, (1 - X)^{2/3} \, \exp(-\alpha X^2) \tag{14}$$

where,

$$k_T = k_I + k_{II} + k_{III} \tag{15}$$

Here, k_I, k_{II}, and k_{III} are rate constants for the individual reactions considered. It is assumed that each of the three reactions occur independently, but that the rate of each is proportional to the same surface area and surface reactivity terms. The term $(1 - X)^{2/3}$ is proportional to the effective surface area undergoing gasification, and the term $\exp(-\alpha X^2)$ represents the relative reactivity of the effective surface area, which decreases with increasing conversion level for positive values of α.

Individual parameters in Equations 14 and 15 are defined as functions of temperature and pressure according to the following expressions:

$$f_L = f_o \, \exp(8467/T_o) \tag{16}$$

$$k_I = \frac{\exp(9.0201 - 31,705/T)\left(1 - \dfrac{P_{CO} P_{H_2}}{P_{H_2O} K_I^E}\right)}{\left[1 + \exp(-22.2160 + 44,787/T)\left(\dfrac{1}{P_{H_2O}} + 16.35 \dfrac{P_{H_2}}{P_{H_2O}} + 43.5 \dfrac{P_{CO}}{P_{H_2O}}\right)\right]^2} \tag{17}$$

$$k_{II} = \frac{P_{H_2}^2 \exp(2.6741 - 33,076/T)\left(1 - \dfrac{P_{CH_4}}{P_{H_2}^2 K_{II}^E}\right)}{\left[1 + P_{H_2}\exp(-10.4520 + 19,976/T)\right]} \tag{18}$$

$$k_{III} = \frac{P_{H_2}^{1/2} P_{H_2O}\exp(12.4463 - 44,544/T)\left(1 - \dfrac{P_{CH_4} P_{CO}}{P_{H_2} P_{H_2O} K_{III}^E}\right)}{\left[1 + \exp(-6.6696 + 15,198/T)\left(P_{H_2}^{1/2} + 0.85\,P_{CO} + 18.62\dfrac{P_{CH_4}}{P_{H_2}}\right)\right]^2} \tag{19}$$

$$\alpha = \frac{52.7\,P_{H_2}}{1 + 54.3\,P_{H_2}} + \frac{0.521\,P_{H_2}^{1/2}\,P_{H_2O}}{10.707\,P_{H_2O} + 0.50\,P_{H_2}^{1/2}\,P_{H_2O}} \tag{20}$$

where,

K_I^E, K_{II}^E, K_{III}^E = equilibrium constants for reactions I, II, and III, considering carbon as graphite

T = reaction temperature, °R

T_o = maximum temperature to which char has been exposed prior to gasification, °R (if $T_o < T$, then a value of $T_o = T$ is used in Equation 16)

P_{H_2}, P_{H_2O},

P_{CO}, P_{CH_4} = partial pressures of H_2, H_2O, CO, and CH_4, atm

f_o = relative reactivity factor for low-rate gasification dependent on the particular carbonaceous solid

Values of f_o obtained in this study were based on the definition $f_o = 1.0$ for a specific batch of air-pretreated Ireland mine coal char. Samples of this coal char obtained from different air-pretreatment tests exhibited some variations in reactivity as determined by thermobalance tests conducted at standard conditions. The values of f_o so determined, ranged from approximately 0.88 to 1.05. Results of tests made with the thermobalance using a variety of coals and coal chars have indicated that the relative reactivity factor, f_o, generally tends to increase with decreasing rank, although

247

individual exceptions to this trend exist.   Values have been obtained
which range from 0.3 for a low-volatile bituminous coal char to about 10 for
a North Dakota lignite.   The reactivity of the Disco char used in gasification
studies conducted by the Consolidation Coal Company[9, 18, 19] is $f_o = 0.488$.

An integrated form of Equation 14 was used to evaluate certain parameters
in the above correlations, based on data obtained with the thermobalance.

$$M(X) = \int_0^X \frac{\exp(+\alpha X^2)\,dX}{(1-X)^{2/3}} = \int_0^{X_R} \frac{\exp(+\alpha X^2)\,dX}{(1-X)^{2/3}} + \int_{X_R}^X \frac{\exp(-\alpha X^2)\,dX}{(1-X)^{2/3}}$$

$$= \int_0^{X_R} \frac{\exp(+\alpha X^2)\,dX}{(1-X)^{2/3}} + f_L k_T t \qquad (21)$$

The term $\displaystyle\int_0^{X_R} \frac{\exp(+\alpha X^2)\,dX}{(1-X)^{2/3}}$ was evaluated from Equation 6 for tests in

which no nitrogen pretreatment was used.   For tests in which the feed coal
char was initially devolatilized in nitrogen at the same temperature and
pressure to be subsequently used for gasification in a gasifying atmosphere,
reactivity for rapid-rate methane formation was destroyed above 1500 °F
and $X_R = 0$.   For this condition —

$$M(X) = \int_0^X \frac{\exp(+\alpha X^2)\,dX}{(1-X)^{2/3}} = f_L k_T t \qquad (22)$$

Typical plots of $M(X)$ versus t are given in Figures 8, 9, and 10 for data
obtained with air-pretreated Ireland mine coal char.   The slopes of the lines
drawn correspond to values of $f_L k_T$ characteristic of each test.   Results of
tests conducted with pure steam (Figure 8) were correlated using $\alpha = 0$
consistent with Equation 20 which corresponds to the situation in which
specific gasification rates, $\frac{dX/dt}{(1-X)}$, increase with an increasing carbon
conversion level.   For gasification in hydrogen or steam-hydrogen mixtures
(Figures 9 and 10), however, specific gasification rates generally decrease
with increasing conversion level.
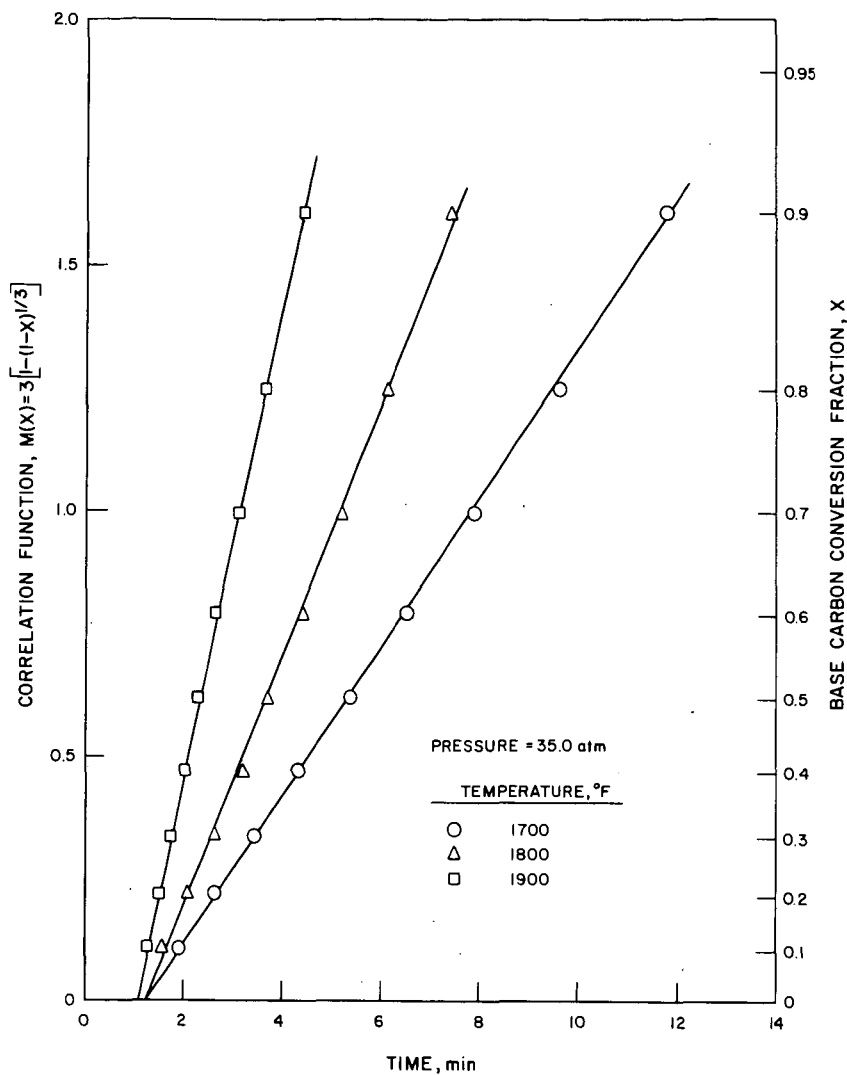
Figure 8.   EFFECT OF TEMPERATURE ON LOW-RATE GASIFICATION
OF AIR-PRETREATED IRELAND MINE COAL CHAR IN STEAM

A-112-1007

249
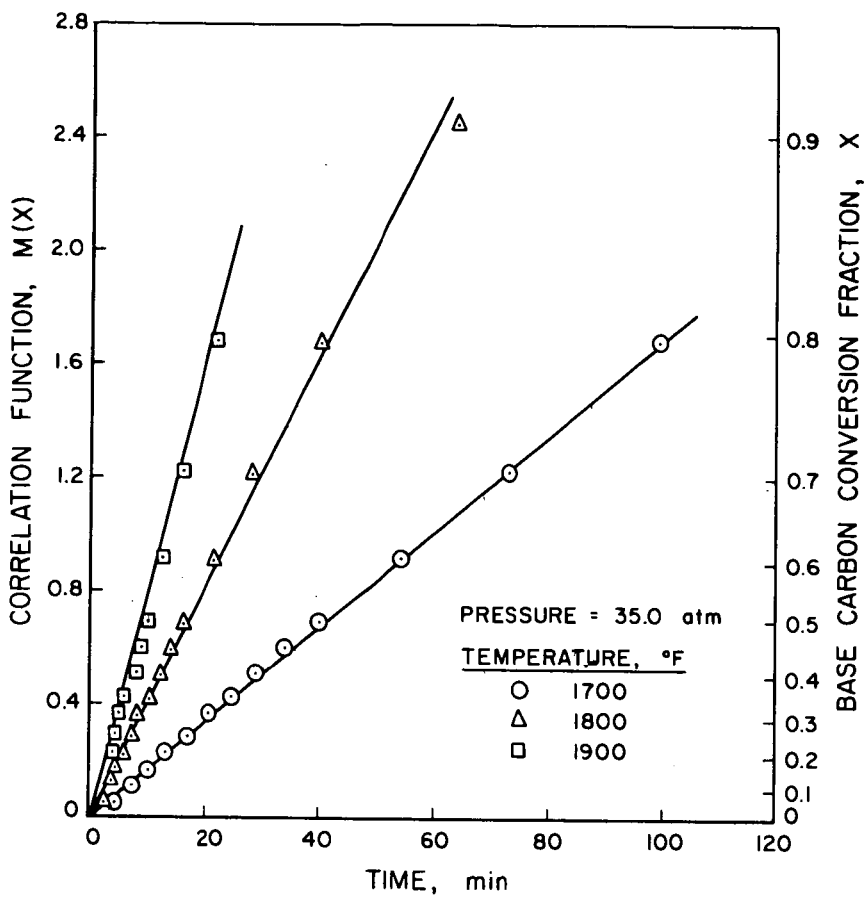
A-112-1003

Figure 9. EFFECT OF TEMPERATURE ON LOW-RATE GASIFICATION
OF AIR-PRETREATED IRELAND MINE COAL CHAR IN HYDROGEN
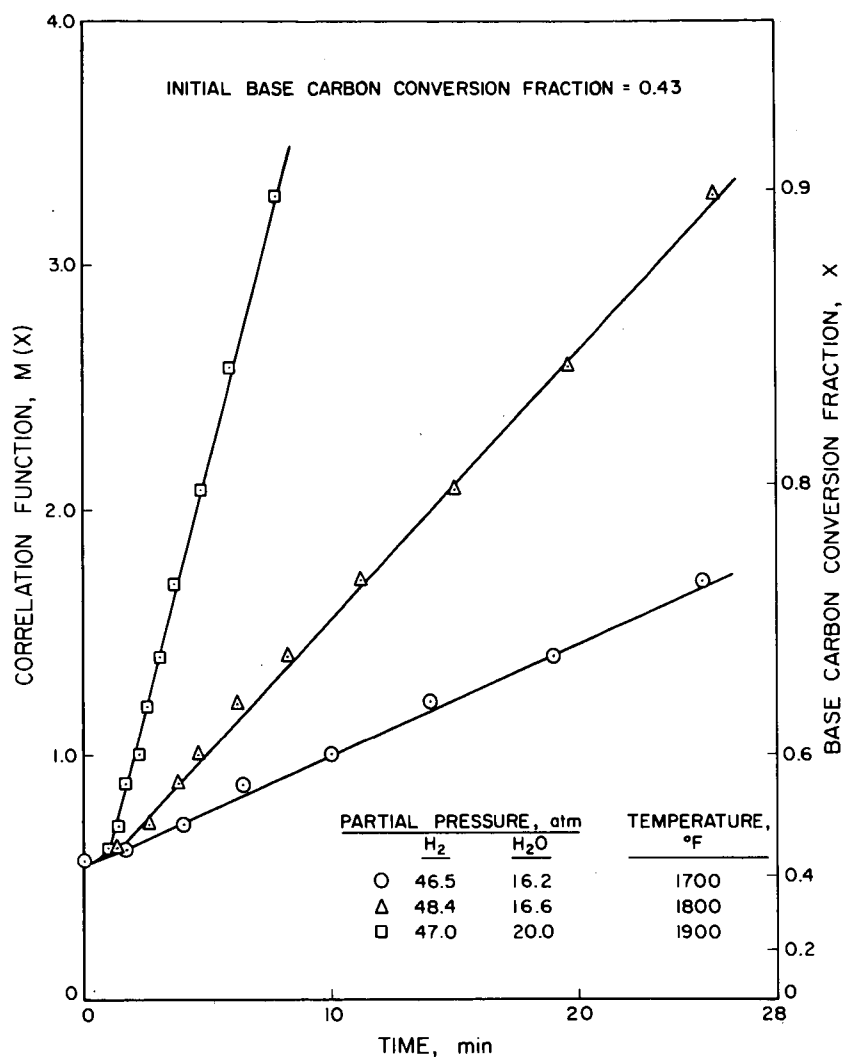
250

Figure 10.   EFFECT OF TEMPERATURE ON LOW-RATE
GASIFICATION OF AIR-PRETREATED IRELAND MINE
COAL CHAR IN STEAM-HYDROGEN MIXTURES

251

Carbon gasification rates were directly measured in the fluid-bed tests conducted with Disco char,[9, 18, 19] and values of $f_L k_T$ and α can be obtained graphically by plotting values of $\ln \frac{dX/dt}{(1-X)^{2/3}}$ versus X^2. Such a plot is illustrated in Figure 11, where the value of $\ln \frac{dX/dt}{(1-X)^{2/3}}$ at $X = 0$ is equal to $f_L k_T$ and the slope of a given line is equal to α. Generally, the correlations presented are consistent with values of $f_L k_T$ and α obtained for the gasification of Disco char at temperatures of 1600° and 1700°F and pressures of 1, 6, and 30 atmospheres for gasification with pure hydrogen and with various steam-hydrogen mixtures. The correlations are also consistent with individual rates of methane and carbon oxide formation reported in the investigations conducted with Disco char for initial levels of carbon conversion. Although the relative rates of methane to carbon oxide formation were reported to increase somewhat with increasing conversion level, a trend not accounted for in the model developed in this study, investigators at the Consolidation Coal Company have suggested that this effect was caused by a catalytic reaction downstream of the fluid-bed reactor employed, in which some of the carbon monoxide produced in the reactor was converted to methane.[5]

The consistency between the calculated and experimental values of $f_L k_T$ for tests conducted at a variety of conditions with the thermobalance using air-pretreated Ireland mine coal char is demonstrated in Tables 2, 3, and 4 and in Figures 12, 13, and 14. The correlations developed have also been used to predict behavior in pilot-scale moving- and fluid-bed tests conducted at IGT and elsewhere. The assumptions made in characterizing the nature of gas-solids contacting in these integral systems have been previously described.[14] The most important assumptions made for fluid-bed systems are a) the gas in the fluid bed is perfectly mixed and b) when continuous solids flow is employed, the solids are in plug flow. For moving-bed systems, we assumed that both gas and solids were in plug flow. With these simplifying assumptions, the conditions of primary importance in

252

Table 2. COMPARISON OF EXPERIMENTAL AND CALCULATED RATE CONSTANTS FOR
GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN HYDROGEN

Temp, °F	Hydrogen Press., atm	Base Carbon Conversion Range, fraction	Rate Constant, $f_L k_T$ min^{-1}	
			Experimental	Calculated
1600	36.5	0-0.314	0.0068	0.0069
1650	36.3	0-0.541	0.0117	0.0112
1650	36.7	0-0.592	0.0111	0.0113
1650	36.7	0-0.654	0.0097	0.0113
1700	19.3	0-0.197	0.0106	0.0090
1700	36.2	0-0.329	0.0167	0.0181
1700	53.2	0-0.449	0.0276	0.0273
1700	69.9	0-0.508	0.0292	0.0365
1700*	35.1	0-0.802	0.0175	0.0175
1750	35.4	0-0.348	0.0261	0.0277
1750	35.4	0-0.509	0.0274	0.0277
1750	36.1	0-0.640	0.0237	0.0283
1750	35.2	0-0.367	0.0272	0.0276
1770*	1.0	0	0	0.0002
1770*	18.1	0-0.069	0.0175	0.0152
1770*	36.6	0-0.134	0.0350	0.0341
1770*	36.1	0-0.570	0.0290	0.0335
1770*	52.9	0-0.180	0.0500	0.0510
1770*	69.9	0-0.250	0.0700	0.0686
1800	21.6	0-0.263	0.0222	0.0239
1800	49.9	0-0.263	0.0641	0.0617
1800*	36.0	0-0.910	0.0416	0.0414
1900*	35.3	0-0.850	0.0910	0.0920

* In these tests, the air-pretreated coal char was either initially devolatilized in nitrogen for 1 hour at the temperature subsequently used for gasification in a gasifying medium, or it was devolatilized and partially gasified in an integral fluid-bed test using a steam-hydrogen feed gas.

253

Table 3. COMPARISON OF EXPERIMENTAL AND CALCULATED RATE CONSTANTS FOR GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN STEAM AND STEAM-HYDROGEN MIXTURES

Temp, °F	Partial Pressure, atm		Base Carbon Conversion Range, fraction	Rate Constant, $f_L k_T$ min^{-1}	
	H_2	H_2O		Experimental	Calculated
1700	--	35.0	0-0.941	0.1547	0.1736
1700	27.3	29.8	0-0.977	0.0598	0.0528
1700	12.8	23.6	0-0.327	0.0706	0.0566
1700	17.8	18.4	0-0.272	0.0365	0.0385
1700	19.2	17.5	0-0.651	0.0356	0.0361
1700	18.2	17.9	0-0.816	0.0344	0.0373
1700	23.3	12.4	0-0.300	0.0339	0.0274
1700	23.2	12.5	0-0.429	0.0262	0.0275
1700	23.8	11.9	0-0.511	0.0190	0.0267
1700	25.0	11.3	0-0.725	0.0224	0.0261
1700 *	13.7	48.5	0.43-0.908	0.0831	0.1110
1700 *	46.5	16.2	0.43-0.781	0.0446	0.0385
1700 **	28.3	32.5	0.43-0.832	0.0425	0.0564
1750	17.6	18.5	0-0.801	0.0526	0.0763
1750	18.3	18.2	0-0.495	0.0613	0.0741
1750	17.6	18.5	0-0.702	0.0667	0.0763
1750	18.0	18.5	0-0.940	0.0917	0.0758
1750	5.3	30.8	0-0.573	0.1803	0.2162
1750	23.2	13.2	0-0.320	0.0441	0.0532
1750	26.9	9.2	0-0.334	0.0406	0.0422
1750	17.6	18.3	0-0.350	0.0670	0.0815
1800	--	35.0	0-0.990	0.2559	0.2815
1800	48.4	16.6	0-0.956	0.1115	0.1130
1800	32.4	27.6	0-0.981	0.1643	0.1710
1900	--	35.0	0-0.992	0.4795	0.4366
1900 *	17.2	42.7	0.43-0.996	0.6570	0.8750
1900 *	47.0	20.0	0.43-0.999	0.4000	0.3900
1900 *	33.2	33.2	0.43-0.997	0.680	0.607

* In these tests, the air-pretreated coal char was either initially devolatilized in nitrogen for 1 hour at the temperature subsequently used for gasification in a gasifying medium, or it was devolatilized and partially gasified in an integral fluid-bed test using a steam-hydrogen feed gas.
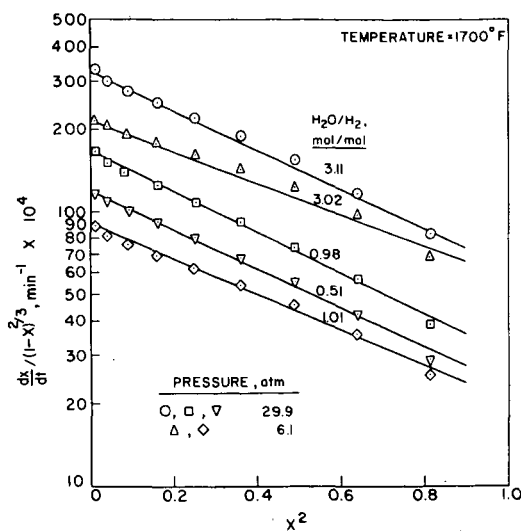
254

Table 4. COMPARISON OF EXPERIMENTAL AND CALCULATED RATE CONSTANTS FOR GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN SYNTHESIS GAS

Temp, °F	Partial Pressure, atm					Base Carbon Conversion Range, fraction	Rate Constant, $f_L k_T$ min^{-1}	
	CO	CO_2	H_2	H_2O	CH_4		Experimental	Calculated
1550	0.17	0.32	5.92	28.11	1.68	0–0.277	0.0045	0.0034
1600	0.95	0.28	14.46	11.07	10.73	0–0.130	0.0002	0.0006
1600	0.65	0.35	12.74	13.82	9.68	0–0.143	0.0007	0.0009
1600	0.65	0.38	14.49	11.33	10.29	0–0.159	0.0006	0.0006
1600	0.17	0.17	7.73	14.66	9.65	0–0.228	0.0022	0.0044
1600	0.10	0.33	6.41	26.58	2.18	0–0.571	0.0146	0.0093
1600	8.60	6.38	11.07	7.50	2.38	0–0.106	0.0001	0.0001
1600	7.57	1.70	18.87	6.84	1.04	0–0.258	0.0022	0.0033
1600	2.28	0.46	19.03	6.57	8.48	0–0.176	0.0004	0.0002
1650	0.55	0.26	11.76	14.66	9.65	0–0.228	0.0026	0.0036
1650	0.10	0.29	6.27	26.47	2.51	0–0.703	0.0234	0.0233
1650	2.24	3.25	6.00	23.02	1.29	0–0.426	0.0089	0.0099
1700	1.85	1.23	8.47	24.71	0.04	0–0.745	0.0272	0.0400
1700	6.05	1.64	15.81	12.91	0.16	0–0.550	0.0122	0.0122
1700	5.27	4.17	10.43	15.87	0.05	0–0.576	0.0143	0.0128
1700	4.52	3.79	9.54	18.11	0.12	0–0.619	0.0166	0.0161
1700	6.90	4.45	10.88	13.58	0.14	0–0.543	0.0125	0.0096
1700	2.26	3.12	3.49	28.07	0.11	0–0.817	0.0516	0.0481
1700	4.33	4.69	4.18	22.54	0.07	0–0.736	0.02680	0.0216
1700**	0.60	2.80	4.30	60.10	0.40	0.43–0.871	0.104	0.128
1700**	5.0	9.4	19.8	25.8	2.1	0.43–0.663	0.0200	0.0169
1700**	1.8	3.1	6.3	19.2	0.4	0.43–0.659	0.0188	0.0274
1700**	5.9	10.8	13.2	28.0	0.9	0.43–0.661	0.0136	0.0172
1700**	4.3	5.1	6.7	16.8	0.5	0.43–0.556	0.0110	0.0117
1750	6.07	4.62	9.69	13.47	2.34	0–0.452	0.0092	0.0095
1750	3.31	4.80	8.12	19.08	1.23	0–0.842	0.0404	0.0315
1750	2.49	3.94	4.99	24.18	0.94	0–0.952	0.0771	0.0588
1750	5.87	6.61	7.03	16.00	0.16	0–0.697	0.0230	0.0217
1750	6.6	4.9	10.6	13.9	0.3	0–0.623	0.0170	0.0175

Table 4, Cont. COMPARISON OF EXPERIMENTAL AND CALCULATED RATE CONSTANTS FOR GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN SYNTHESIS GAS

Temp, °F	Partial Pressure, atm					Base Carbon Conversion Range, fraction	Rate Constant, $f_L k_T$ min^{-1}	
	CO	CO$_2$	H$_2$	H$_2$O	CH$_4$		Experimental	Calculated
1800*	6.2	7.4	18.1	31.6	0.3	0.43-0.933	0.0880	0.0880
1800*	1.8	4.9	11.6	47.7	0.2	0.43-0.979	0.236	0.248
1800*	10.7	6.7	17.7	19.1	1.5	0.43-0.776	0.043	0.0300
1800*	4.5	2.6	7.4	13.3	0.3	0.43-0.784	0.0395	0.0448
1800*	6.9	3.4	10.7	8.4	0.4	0.43-0.678	0.0229	0.0193
1800*	6.0	9.7	13.4	30.5	0.4	0.43-0.878	0.0736	0.0849
1800*	2.9	11.1	14.1	36.5	0.4	0.43-0.899	0.105	0.146
1800*	5.9	4.9	7.6	14.1	0.2	0.43-0.771	0.0431	0.0389
1800*	1.1	3.3	4.3	24.7	0.2	0.43-0.959	0.182	0.199
1800*	12.9	4.9	7.5	9.4	0.3	0.43-0.647	0.0111	0.0101
1800*	0.5	2.0	4.0	27.4	0.1	0.43-0.892	0.246	0.268
1800*	--	1.2	2.6	30.1	0.1	0.43-0.914	0.273	0.271
1900*	4.0	7.4	18.0	35.7	0.2	0.43-0.998	0.391	0.395
1900*	3.2	5.3	11.8	42.9	0.1	0.43-0.991	0.579	0.513
1900*	12.3	7.8	23.7	16.0	1.3	0.43-0.845	0.0820	0.0964
1900*	3.9	2.9	8.8	11.9	0.1	0.43-0.956	0.141	0.169
1900*	7.1	3.3	11.4	7.9	0.2	0.43-0.840	0.0638	0.0713
1900*	1.5	3.1	6.6	20.7	0.2	0.43-0.981	0.364	0.415
1900*	8.9	10.5	15.2	28.2	0.5	0.43-0.999	0.227	0.200
1900*	19.2	11.6	16.6	15.5	0.7	0.43-0.824	0.0721	0.0609
1900*	3.8	7.8	11.0	41.0	0.3	0.43-1.009	0.438	0.442
1900*	6.1	5.3	8.3	13.5	0.1	0.43-0.984	0.191	0.142
1900*	1.4	3.7	4.7	23.7	0.1	0.43-1.033	0.500	0.471
1900*	10.6	5.2	8.4	10.5	0.1	0.43-0.872	0.085	0.064
1900*	0.3	1.3	2.7	29.7	--	0.43-1.028	0.655	0.817
1900*	1.0	3.3	7.0	56.7	0.1	0.43-1.001	1.000	0.892
2000*	3.2	5.3	13.4	46.1	0.2	0.43-0.991	1.36	1.27
2000*	7.5	6.0	18.6	35.8	0.5	0.43-1.047	0.771	0.873
2000*	0.8	0.3	33.9	32.5	0.5	0.43-0.987	1.462	1.297

* In these tests, the air-pretreated coal char was either initially devolatilized in nitrogen for 1 hour at the temperature subsequently used for gasification in a gasifying medium, or it was devolatilized and partially gasified in an integral fluid-bed test using a steam-hydrogen feed gas.
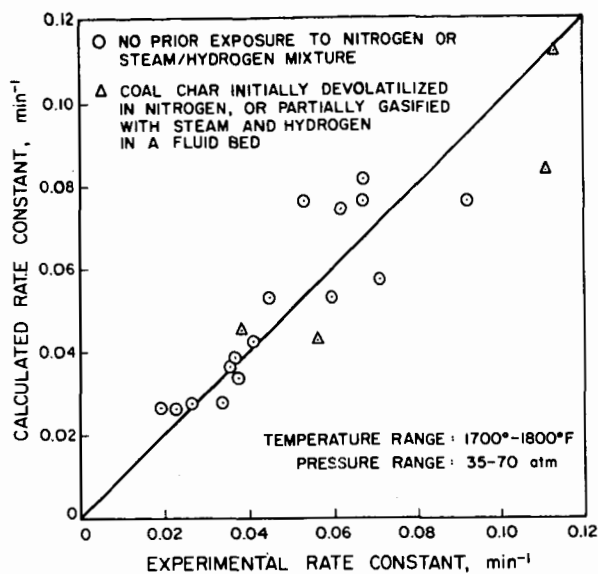
Figure 11. EFFECTS OF PRESSURE AND GAS COMPOSITION ON
LOW-RATE GASIFICATION OF DISCO CHAR IN
STEAM-HYDROGEN MIXTURES[9, 19]
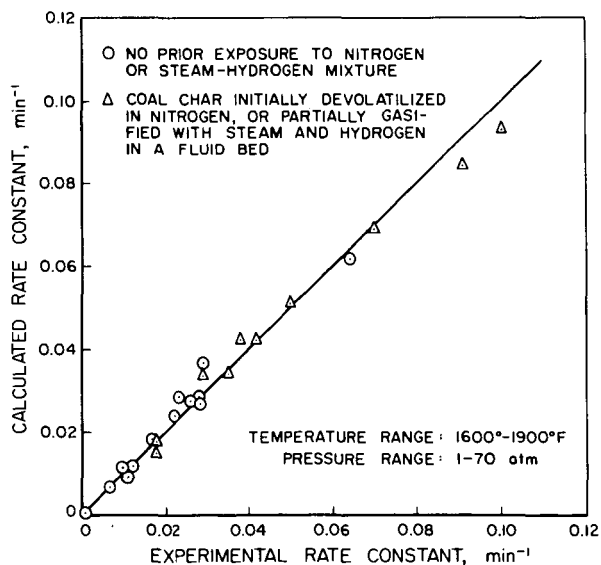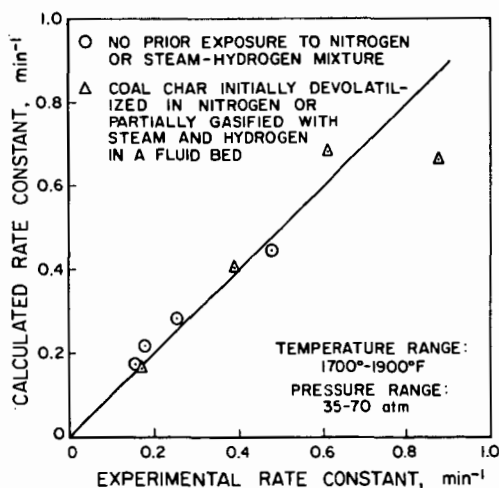

Figure 12. COMPARISON OF EXPERIMENTAL AND CALCULATED
RATE CONSTANTS FOR LOW-RATE GASIFICATION OF
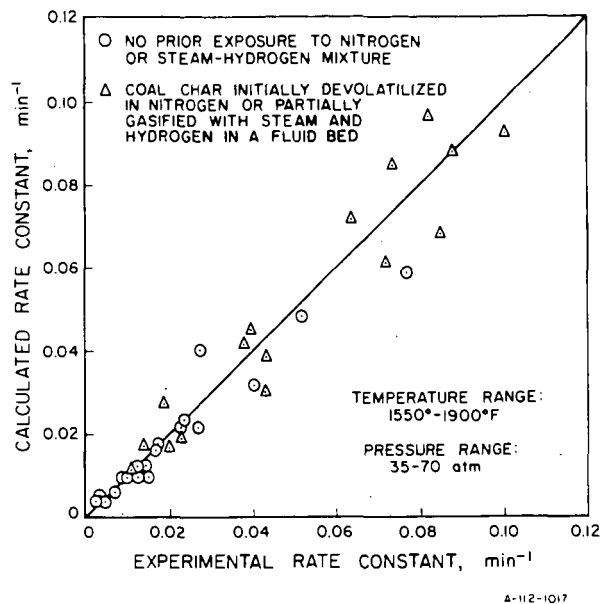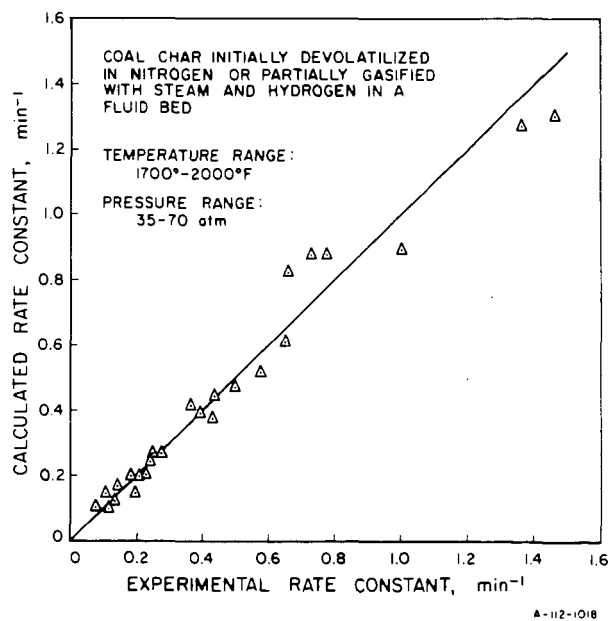AIR-PRETREATED IRELAND MINE COAL CHAR IN HYDROGEN

257

(a)

(b)

Figure 13. COMPARISON OF EXPERIMENTAL AND CALCULATED
RATE CONSTANTS FOR LOW-RATE GASIFICATION OF
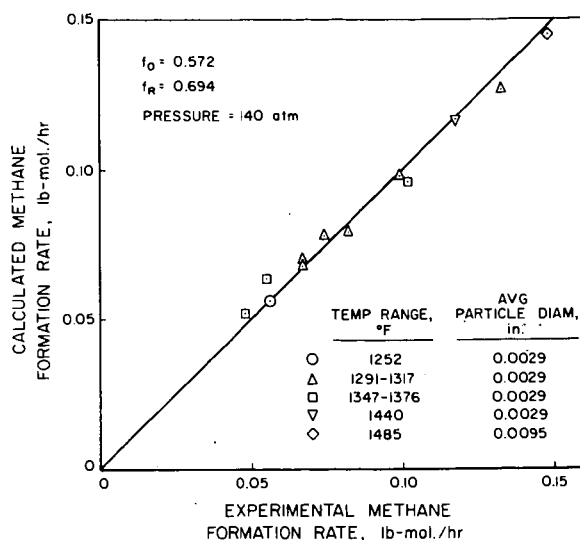AIR-PRETREATED IRELAND MINE COAL CHAR
IN STEAM-HYDROGEN MIXTURES

258

(a)

A-112-1017

(b)

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Figure 14.   COMPARISON OF EXPERIMENTAL AND CALCULATED
RATE CONSTANTS FOR LOW-RATE GASIFICATION OF
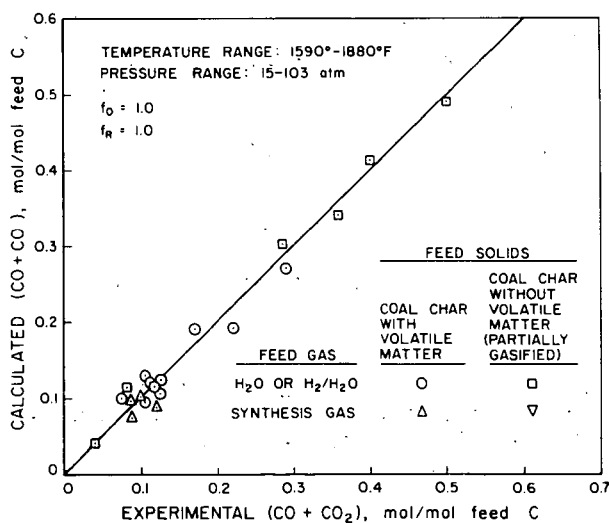AIR-PRETREATED IRELAND MINE COAL CHAR IN SYNTHESIS GASES

259

characterizing integral gasification behavior in individual tests include coal char feed rate and composition, particle residence times in the reactor, reactor temperature, pressure, feed gas composition, and flow rate. For cases where coal char containing volatile matter was used as a feed material, rapid-rate methane formation and devolatilization were assumed to occur in a free-fall space above the reaction beds employed in the systems. When devolatilized coal char was the feed material, no rapid-rate methane formation was considered to occur. Predicted and experimental integral rates of carbon oxides and methane formation are compared in Figures 15-19, which show good agreement for a wide range of experimental conditions.

Frequently, the $P_{CH_4}/P_{H_2}^2$ ratio in product gases from integral fluid-bed systems for the gasification of coal or coal char with steam-hydrogen containing gases is greater than the equilibrium constant for the graphite-hydrogen-methane system. This has often been interpreted as corresponding to a situation in which the coal or coal char has a thermodynamic activity greater than unity with respect to graphite. The models proposed in this paper offer two other explanations for this phenomenon: Rapid-rate methane formation occurs when coal or coal char containing volatile matter is used as a feed material. The methane yield resulting from this step is kinetically determined, independent of methane's partial pressure. Under certain conditions then, values of the ratio, $P_{CH_4}/P_{H_2}^2$, greater than that corresponding to the equilibrium for the graphite-hydrogen-methane system can result. Values of the $P_{CH_4}/P_{H_2}^2$ ratio greater than that corresponding to the equilibrium considered can also occur for low-rate gasification of coal char according to the model assumed in this study. This is illustrated in Figure 20, where the results shown were based on computations of gas yields in a hypothetical fluid-bed for char gasification with a pure steam feed gas, using the correlations described above. The reason for the behavior illustrated is that, at intermediate values of hydrogen partial pressure, the rate of Reaction III, which produces methane, is greater than the reverse rate of Reaction II in which methane is consumed when a potential for carbon deposition by this

260

Figure 15 chart:

CALCULATED METHANE FORMATION RATE, lb-mol./hr

$f_0 = 0.572$
$f_R = 0.694$
PRESSURE = 140 atm

|	TEMP RANGE, °F	AVG PARTICLE DIAM, in.
○	1252	0.0029
△	1291-1317	0.0029
□	1347-1376	0.0029
▽	1440	0.0029
◇	1485	0.0095

EXPERIMENTAL METHANE FORMATION RATE, lb-mol./hr

A-112-1020

Figure 15. COMPARISON OF EXPERIMENTAL AND CALCULATED INTEGRAL RATES OF METHANE FORMATION FOR HYDROGENATION OF MONTOUR BITUMINOUS COAL CHAR (17% Volatile Matter) IN A MOVING-BED REACTOR (IGT Study)

Figure 16 chart:

CALCULATED (CO + CO), mol/mol feed C

TEMPERATURE RANGE: 1590°-1880°F
PRESSURE RANGE: 15-103 atm
$f_0 = 1.0$
$f_R = 1.0$

	FEED SOLIDS	
FEED GAS	COAL CHAR WITH VOLATILE MATTER	COAL CHAR WITHOUT VOLATILE MATTER (PARTIALLY GASIFIED)
H_2O OR H_2/H_2O	○	□
SYNTHESIS GAS	△	▽

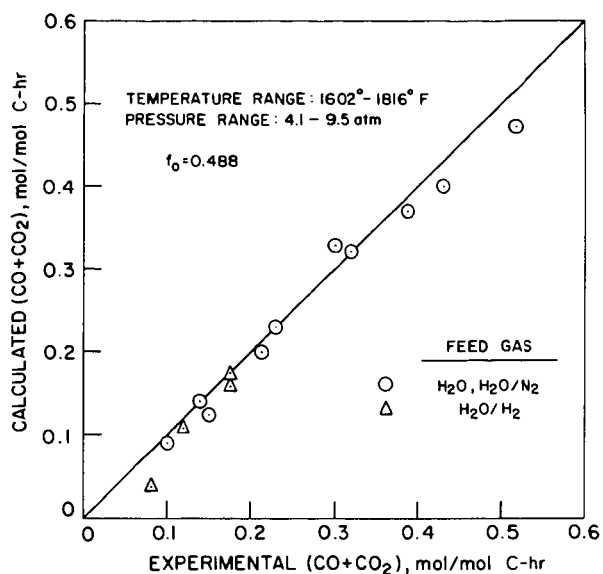EXPERIMENTAL $(CO + CO_2)$, mol/mol feed C

A-112-1021

Figure 16. COMPARISON OF EXPERIMENTAL AND CALCULATED INTEGRAL RATES OF CARBON OXIDES FORMATION FOR GASIFICATION OF AIR-PRETREATED IRELAND MINE COAL CHAR IN 2-, 4-, AND 6-INCH-INSIDE-DIAMETER FLUID-BED REACTORS (IGT Studies)
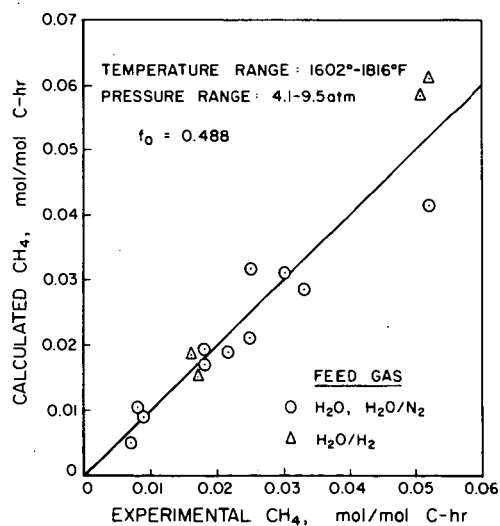
261
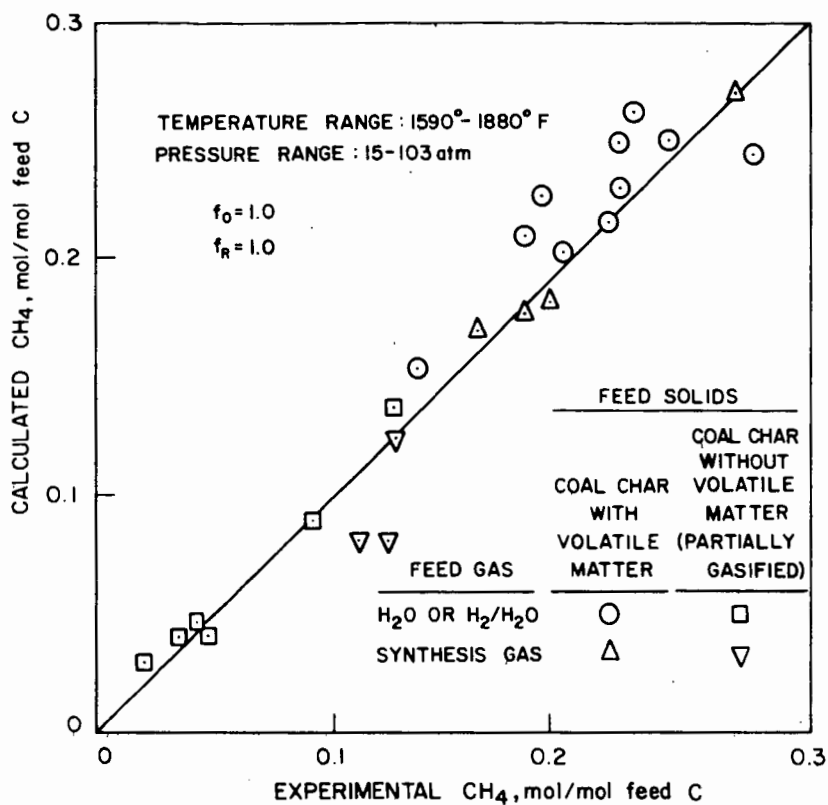
A-112-1014

Figure 17.   COMPARISON OF EXPERIMENTAL AND CALCULATED
INTEGRAL RATES OF METHANE FORMATION FOR GASIFICATION
OF AIR-PRETREATED IRELAND MINE COAL CHAR IN 2-, 4-, AND
6-INCH-INSIDE-DIAMETER FLUID-BED REACTORS (IGT Studies)

Figure 18.   COMPARISON OF EXPERIMENTAL AND CALCULATED
INTEGRAL RATES OF CARBON OXIDES FORMATION FOR
GASIFICATION OF DISCO CHAR IN A FLUID-BED REACTOR[12]

Figure 19.   COMPARISON OF EXPERIMENTAL AND CALCULATED
INTEGRAL RATES OF METHANE FORMATION FOR
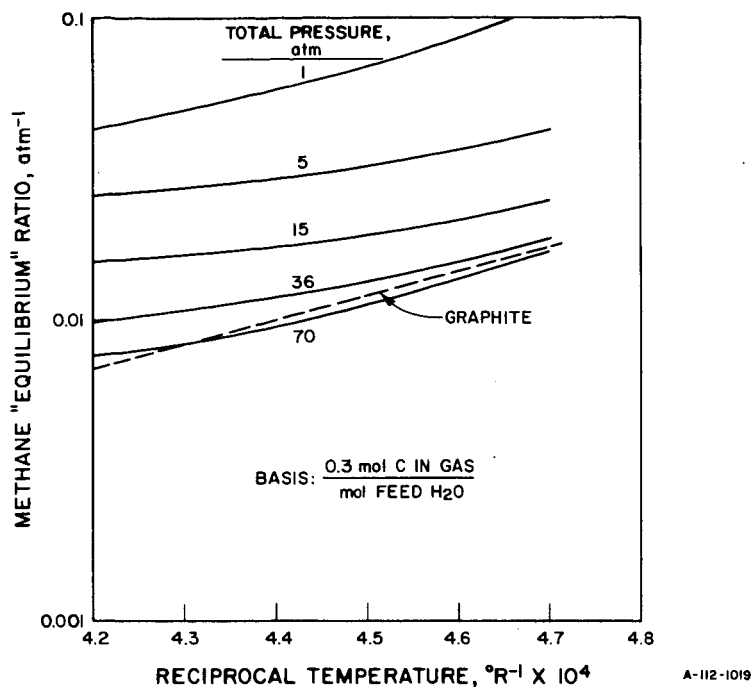GASIFICATION OF DISCO CHAR IN A FLUID-BED REACTOR[12]

263

Figure 20. CALCULATED VARIATIONS OF THE METHANE "EQUILIBRIUM" RATIO $(P_{CH_4}/P^2_{H_2})$ FOR GASIFICATION OF CARBON WITH STEAM IN A BACKMIXED REACTOR

reaction exists. The partial pressure dependencies defined in the correlations developed are such, however, that, at sufficiently high hydrogen partial pressures, Reaction II dominates and equilibrium for this reaction is approached.

The qualitative trends exhibited in Figure 20 and even the magnitudes of these trends bear a striking resemblance to a similar plot given by Squires[15] to correlate the activities of coals and chars for equilibrium in the char-hydrogen-methane system with temperature and pressure.

SUMMARY OF NOTATION

A	= nongasifiable matter in feed coal char (including ash and some sulfur), g/g feed coal char
C_b	= base carbon in coal char at an intermediate gasification level, g/g feed coal char
C_b^o	= carbon in the fixed carbon fraction of the feed coal char as determined by a proximate analysis, g/g feed coal char
C_t^o	= total carbon in the feed coal char as determined by an ultimate analysis, g/g feed coal char
C_v	= volatile carbon in feed coal, g/g feed coal char
f_o	= relative reactivity factor for low-rate gasification dependent on the particular carbonaceous solid
f_L	= relative reactivity factor for low-rate gasification dependent on the particular carbonaceous solid and pretreatment temperature
f_R	= relative reactivity factor for rapid-rate methane formation, dependent on the particular carbonaceous solid
k_T	= overall rate constant for low-rate gasification, min^{-1}
$k_{2(T)}$, $k_{3(T)}$	= rate constants, min^{-1}
k_I, k_{II}, k_{III}	= rate constants for Reactions I, II, and III, min^{-1}
K_I^E, K_{II}^E, K_{III}^E	= equilibrium constants for Reactions I, II, and III considering carbon as graphite
N_{A_o}	= concentration of species A_o at any time, mol/mol base carbon
$N_{A_o}^o$	= initial concentration of species A_o, mol/mol base carbon
N_{A_*}	= concentration of species A_* at any time, mol/mol base carbon
P_{H_2}, P_{H_2O}, P_{CO}, P_{CO_2}, P_{CH_4}	= partial pressures of H_2, H_2O, CO, CO_2 and CH_4, atm

265

t	= time, min
T	= reaction temperature, °R
T_o	= pretreatment temperature, °R
V	= volatile matter in feed coal char (including moisture), g/g feed coal char
W_o	= weight of feed coal char, g
ΔW	= weight loss of coal char during gasification, g
X	= total base carbon conversion fraction
X_R	= base carbon conversion fraction after reaction in rapid-rate methane formation stage is completed

Greek Symbols

α	= kinetic parameter, dependent on gas composition and pressure
β	= $k_3(T)/k_2(T)$ ratio
γ	= noncarbon matter evolved along with base carbon, g/g base carbon evolved

ACKNOWLEDGMENT

REFERENCES CITED

1. Birch, T. J., Hall, K. R. and Urie, R. W., "Gasification of Brown Coal With Hydrogen in a Continuous Fluidized-Bed Reactor," J. Inst. Fuel 33, 422-35 (1960) September.

2. Blackwood, J. D., "The Reaction of Carbon With Hydrogen at High Pressure," Aust. J. Chem. 12, 14-28 (1959) February.

3. Blackwood, J. D. and McCarthy, D. J., "The Mechanism of Hydrogenation of Coal to Methane," Aust. J. Chem. 19, 797-813 (1966) May.

4. Blackwood, J. D. and McGrory, F., "The Carbon-Steam Reaction at High Pressure," Aust. J. Chem. 11, 16-33 (1958) February.

5. Curran, G. and Gorin, E., "Phase II, Bench-Scale Research on CSG Process — Laboratory Physicochemical Studies," U. S. Office of Coal Research R&D Report No. 16, Interim Report No. 3, Book 2, Washington, D.C.: U. S. Government Printing Office, 1970.

6. Eddinger, R. T., Freidman, L. D. and Rau, A., "Devolatilization of Coal in a Transport Reactor," Fuel 19, 245-52 (1966).

7. Feldmann, H. F., et al., "Reaction Model for Bituminous Coal Hydrogasification in a Dilute Phase." Paper presented at the 160th National Meeting of the American Chemical Society, Division of Petroleum Chemistry, Chicago, September 13-18, 1970.

8. Goring, G. E., et al., "Kinetics of Carbon Gasification by Steam: Effect of High-Temperature Pretreatment on Reactivity of Low-Temperature Char to Steam and Carbon Dioxide," Ind. Eng. Chem. 44, 1051-57 (1952) May.

9. Goring, G. E., et al., "Kinetics of Carbon Gasification by Steam: Mechanism of Interaction of Low-Temperature Char and Steam-Hydrogen Mixtures at 1600°F," Ind. Eng. Chem. 45, 2586-91 (1953) November.

10. Hiteshue, R. W., Friedman, S. and Madden, R., "Hydrogasification of a High-Volatile A Bituminous Coal," U. S. Bur. Mines Rep. Invest. No. 6376 (1964).

11. Kimber, G. M. and Gray, M. D., "Rapid Devolatilization of Small Coal Particles," J. Combust. Flame Inst. 2, 360-62 (1967) August.

12. May, W. G., Mueller, R. H. and Sweetser, S. B., "Carbon-Steam Reaction Kinetics From Pilot Plant Data," Ind. Eng. Chem. 50, 1289-96 (1958) September.

13. Mosely, F. and Patterson, D., "The Rapid High-Temperature Hydrogenation of Coal Chars. Part 2: Hydrogen Pressures up to 1000 Atmospheres," J. Inst. Fuel 38, 378-91 (1965) September.

14. Pyrcioch, E. J., Feldkirchner, H. L., Tsaros, C. L., Johnson, J. L., Bair, W. G., Lee, B. S., Schora, F. C., Huebler, J. and Linden, H. R., "Production of Pipeline Gas by Hydrogasification of Coal," IGT Res. Bull. No. 39. Chicago, November 1972.

15. Squires, A. M., "Steam-Oxygen Gasification of Fine Sizes of Coal in Fluidized Bed at Elevated Pressure. I. Reaction of Carbon With Hydrogen," Trans. Inst. Chem. Eng. 39, 3-9 (1961); II. "Reaction of Carbon With Steam," ibid., 10-15 (1961); III. "Relation of Integral to Differential Rates: Effect of Carbon Level on Gasification Rate and Role of the Shift Reaction," ibid., 16-21 (1961).

16. Wen, C. Y. and Huebler, J., "Kinetic Study of Coal-Char Hydrogasification — Rapid Initial Reaction," _Ind. Eng. Chem. Process Des. Dev._ 4, 147-54 (1965) April.

17. Zahradnick, R. I. and Glenn, R. A., "Direct Methanation of Coal." Paper presented at 158th National Meeting of the American Chemical Society, Division of Fuel Chemistry, New York, September 7-12, 1969.

18. Zielke, C. W. and Gorin, E., "Kinetics of Carbon Gasification. Interaction of Hydrogen With Low-Temperature Char at 1500° to 1700°F," _Ind. Eng. Chem._ 47, 820-25 (1955) April.

19. Zielke, C. W. and Gorin, E., "Kinetics of Carbon Gasification," _Ind. Eng. Chem._ 49, 396-403 (1957) March.